

Stiff Quantum Polymers

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At ultralow temperatures, polymers exhibit quantum behavior, which is calculated here for the second and fourth moments of the end-to-end distribution in the large-stiffness regime. The result should be measurable for polymers in wide optical traps.

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1. Present-day laser techniques make it possible to build optical traps, and lattices of traps, in which one can host a variety of atoms or molecules and study their behavior at very low temperatures. Gases of bosons, fermions, and their simple bound states have been investigated in this way with interesting insights into the quantum physics of many-body systems [1]. In this note we would like to propose to use these traps for the study of the quantum behavior of stiff polymers. The low temperatures can be reached by buffergas cooling with He which permits reaching temperatures of the order of mK. This should in be possible, for example, with carbohydrates or polyacetylene. We shall assume the traps to be much wider than the length of the polymer so that we may ignore the distortions coming from the trap potential.

The end-to-end distribution $P_L(\mathbf{R})$ of a polymer of length L contains information on various experimentally observable properties, in particular the moments

$$\langle R^m \rangle = S_D \int_0^\infty dR R^{D-1} R^m P_L(\mathbf{R}), \quad (1)$$

where $S_D = 2\pi^{D/2}/\Gamma(D/2)$ is the surface of a unit sphere in D dimensions. The classical temperature behavior of these moments is well known [2, 3]. Here we shall calculate the modifications caused by quantum fluctuations.

Let us briefly recall the calculation of the classical end-to-end distribution in the Kratky-Porod chain with N links of length a in D dimensions [2, 3]. Its bending energy is

$$E_{\text{bend}}^N = \frac{\kappa a}{2} \sum_{n=1}^{N-1} (\nabla \mathbf{u}_n)^2, \quad (2)$$

where κ the stiffness, \mathbf{u}_n are unit vectors on a sphere in D dimensions specifying the directions of the polymer links, and $\nabla \mathbf{u}_n \equiv (\mathbf{u}_{n+1} - \mathbf{u}_n)/a$ is the difference between neighboring \mathbf{u}_n 's. The initial and final link directions have a distribution

$$P(\mathbf{u}_2, \mathbf{u}_1 | L) \equiv (\mathbf{u}_b L | \mathbf{u}_a 0) = \int \mathcal{D}^D \mathbf{u} e^{-\beta E_{\text{bend}}^N}, \quad (3)$$

where $\mathcal{D}^D \mathbf{u}$ is the product of integrals over the unit spheres of \mathbf{u}_n ($n = 2, \dots, N-1$), and $\beta \equiv 1/k_B T$

(T =temperature, k_B = Boltzmann constant). The normalization is irrelevant and will be fixed at the end.

2. If L denotes the length of the polymer, the bending energy reads $E_{\text{bend}}^L = \kappa \int_0^L ds (\partial_s \mathbf{u})^2 / 2$. Then the probability (3) coincides with the Euclidean path integral of a particle on the surface of a unit sphere. The end-to-end distance in space is $\mathbf{R} = \int_0^L ds \mathbf{u}(s)$, and its distribution is given by the path integral

$$P_L(\mathbf{R}) \propto \int \mathcal{D}^D \mathbf{u} \delta^{(D)}(\mathbf{R} - L \mathbf{u}_0) e^{-\bar{\kappa} \int_0^L ds \mathbf{u}'^2(s)/2}, \quad (4)$$

where $\bar{\kappa} \equiv \beta \kappa$ and $\mathbf{u}_0 \equiv L^{-1} \int_0^L ds \mathbf{u}(s)$. Introducing the dimensionless vectors \mathbf{q}^T transverse to \mathbf{R} , we parametrize \mathbf{u} as $(\mathbf{q}, \sqrt{1 - \mathbf{q}^2})$ and see that the δ -function enforces

$$\int_0^L ds \mathbf{q}(s) = 0, \quad R = L - \int_0^L ds [\mathbf{q}^2(s)/2 + \dots]. \quad (5)$$

At large stiffness, the distribution can be calculated from the one-loop approximation to the path integral which leads to the Fourier integral [3, 4]

$$P_{L,\beta}(\mathbf{R}) \underset{\text{small } \beta}{\propto} \int_{-i\infty}^{i\infty} \frac{dk^2}{2\pi i} e^{\beta \kappa k^2 (L-R)} F_{L,0}(k^2 L^2) \quad (6)$$

where $F_{L,0}(k^2 L^2)$ is the partition function

$$\begin{aligned} F_{L,0}(k^2 L^2) &\equiv \int_{\text{NBC}} \mathcal{D}'^{D-1} \mathbf{q}^T e^{-(\beta \kappa a/2) \sum_{n=1}^N [(\nabla \mathbf{q})_n^T + k^2 \mathbf{q}_n^T]^2} \\ &\propto \left[\frac{\prod_{n=1}^\infty |K_n|^2}{\prod_{n=1}^\infty (|K_n|^2 + k^2)} \right]^{\frac{D-1}{2}} = \left(\frac{N \sinh \tilde{k} a}{\sinh \tilde{k} L} \right)^{\frac{D-1}{2}}, \end{aligned} \quad (7)$$

with \tilde{k} defined by $\sinh \tilde{k} a = ka$ [5]. The symbol NBC indicates that the open ends of the path integral may be accounted for by Neumann boundary conditions [6].

For a classical polymer, we may use the model in the continuum limit where $a \rightarrow 0$. Then \mathbf{u}_n is replaced by the tangent vector $\mathbf{u}(s) = \partial_s \mathbf{x}(s)$ of the space curve $\mathbf{x}(s)$ of the polymer, where s is the distance of the link from one of the endpoints measured along the polymer. In this

limit, $\tilde{k}L$ coincides with $kL \equiv \bar{k}$, and the right-hand side of (7) can be expanded as in a power series of k :

$$F_{L,0}(\bar{k}^2) = 1 - \frac{D-1}{2^2 \cdot 3} \bar{k}^2 + \frac{(D-1)(5D-1)}{2^5 \cdot 3^2 \cdot 5} \bar{k}^4 + \dots \quad (8)$$

Inserting this into (6) and setting $r \equiv R/L$, we may calculate the unnormalized moments $\langle r^m \rangle = \int dr r^{D-1+m} P_{L,\beta}$ from the integrals

$$\langle r^m \rangle = \int dz (1+z)^{D-1+m} f(\hat{k}^2) \delta(z), \quad (9)$$

where $\hat{k}^2 L^2$ is the differential operator $-(L/\beta\kappa)\partial_z = [-2l/(D-1)]\partial_z$, and $l \equiv (D-1)L/\beta\kappa$ is the *flexibility* of the polymer. From this we find

$$\begin{aligned} \langle r^0 \rangle &= \mathcal{N} \left[1 - \frac{D-1}{6} l + \frac{(5D-1)(D-2)}{360} l^2 + \dots \right], \\ \langle r^2 \rangle &= \mathcal{N} \left[1 - \frac{D+1}{6} l + \frac{(5D-1)D(D+1)}{360(D-1)} l^2 + \dots \right], \quad (10) \\ \langle r^4 \rangle &= \mathcal{N} \left[1 - \frac{D+3}{6} l + \frac{(5D-1)(D+2)(D+3)}{360(D-1)} l^2 + \dots \right], \end{aligned}$$

where \mathcal{N} is some constant. Dividing these by $\langle r^0 \rangle$, we arrive at the normalized moments [7]

$$\langle r^2 \rangle = 1 - \frac{1}{3} l + \frac{13D-9}{180(D-1)} l^2 + \dots, \quad (11)$$

$$\langle r^4 \rangle = 1 - \frac{2}{3} l + \frac{23D-11}{90(D-1)} l^2 + \dots \quad (12)$$

3. Quantum effects are now taken into account by adding for each mass point of the polymer at \mathbf{x}_n a kinetic action

$$\mathcal{A}_{\text{kin}} \equiv \frac{M}{2} \int_0^{\hbar\beta} dt [\dot{\mathbf{x}}_n(t)]^2, \quad (13)$$

where M is the mass. Since $\mathbf{u}_n(t) = \nabla \mathbf{x}_n(t)$, the Euclidean action with time $\tau = it$ reads

$$\mathcal{A} = \frac{\kappa a}{2} \int_0^{\hbar\beta} d\tau \sum_{n=1}^N \left[g^{-2} (\partial_\tau \nabla^{-1} \mathbf{u}_n)^2 + (\nabla \mathbf{u}_n)^2 \right], \quad (14)$$

where $g \equiv \sqrt{\kappa a/M}$, and $F_{L,0}(\bar{k}^2)$ is replaced by $F_{L,\beta}(\bar{k}^2) = e^{-(D-1)\Gamma_{L,\beta}(\bar{k}^2)}$ with

$$\Gamma_{L,\beta}(\bar{k}^2) = \frac{1}{2} \text{Tr} \log [-g^{-2} \partial_\tau^2 (\nabla \bar{\nabla})^{-1} - \nabla \bar{\nabla} + k^2]. \quad (15)$$

The eigenvalues of $i\partial_\tau$ are the Matsubara frequencies $\omega_m = 2\pi m/\hbar\beta$, ($m = 0, \pm 1, \pm 2, \dots$), leading to the finite-temperature generalization of (7):

$$F_{L,0}(\bar{k}^2) = \left[\frac{\prod_{m,n} (g^{-2} \omega_m^2 + |K_n|^4)}{\prod_{m,n} (g^{-2} \omega_m^2 + |K_n|^4 + k^2 |K_n|^2)} \right]^{(D-1)/2}. \quad (16)$$

Performing the product over the m 's, we arrive at

$$F_{L,\beta}(k) = \prod_{n=1}^{\infty} \left[\frac{\sinh K_n^2 \hbar g \beta / 2}{\sinh \sqrt{K_n^4 + k^2 |K_n|^2} \hbar g \beta / 2} \right]^{D-1}. \quad (17)$$

4. In the product (17) we perform an expansion in powers of $\bar{k} \equiv kL$, and find

$$F_{L,\beta}(\bar{k}) = \exp[(D-1)(f_1 \bar{k}^2 + f_2 \bar{k}^4 + \dots)], \quad (18)$$

where

$$f_1(b) = -\frac{b}{4\pi^2} \sum_{n=1}^{\infty} \coth \frac{n^2 b}{2}, \quad (19)$$

$$f_2(b) = \frac{b^2}{32\pi^4} \sum_{n=1}^{\infty} \left[\frac{2}{bn^2} \coth \frac{n^2 b}{2} + \left(\coth^2 \frac{n^2 b}{2} - 1 \right) \right]. \quad (20)$$

The parameter b is the reduced inverse temperature $b \equiv \pi^2 \hbar g / k_B T L^2$.

As a cross check of the above results we go to the high-temperature limit where $\coth(n^2 b/2) \rightarrow 2/n^2 b$ and thus $f_1(b) \rightarrow -1/12$, $f_2(b) \rightarrow 1/360$. Inserting these into (18), we recover (8).

Quantum behavior sets in if b becomes larger than unity. To estimate when this happens we measure the lengths a, L in Å, the mass M in units of the proton mass, the temperature T in mK, and the constant g in units of Å²/sec, we find that $b \approx 7.380 \times 10^6 \sqrt{\kappa a/A} / T L^2$, where A is the atomic number M . In these natural units, κ, a, T , are of order unity, experimentalists should be able to observe the quantum behavior for not too long chains.

At very low temperatures where quantum effects become most visible we find the asymptotic behavior

$$f_2(b) \rightarrow \frac{b}{16\pi^4} \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{b}{96\pi^2}. \quad (21)$$

In this regime, the sum in $f_1(b)$ diverges linearly. It is made finite by remembering that we are dealing with the continuum limit of a discrete polymer with $N = L/a$ links. Hence we must carry the sum only to $n = N$, and obtain

$$f_1(b) \rightarrow -\frac{b}{4\pi^2} \sum_{n=1}^N 1 = -\frac{b}{4\pi^2} N. \quad (22)$$

Setting $r-1 \equiv z$, we replace $(\bar{k}^2)^n$ in Eq. (18) by $[-2l/(D-1)]^n \partial_z^n \delta(z)$, and insert the resulting expansion into the integral $\int dz (1+z)^{D-1+m}$ to find the unnormalized moments of r^0, r^2, r^4 at zero temperature. From their ratios we obtain the normalized moments:

$$\langle r^2 \rangle = 1 + 4l f_1 + l^2 \left(4f_1^2 + 8 \frac{2D-1}{D-1} f_2 \right) + \dots, \quad (23)$$

$$\langle r^4 \rangle = 1 + 8l f_1 + l^2 \left(24f_1^2 + 16 \frac{2D+1}{D-1} f_2 \right) + \dots \quad (24)$$

From these we find

$$\langle 1 - r \rangle = -2lf_1 - 8l^2f_2 + \dots, \quad (25)$$

$$\langle (1 - r)^2 \rangle = l^2 \left(4f_1^2 + \frac{8}{D-1}f_2 \right) + \dots, \quad (26)$$

and the cumulant

$$\langle (1 - r)^2 \rangle_c = l^2 \frac{8}{D-1}f_2 - 32l^3f_1f_2 - 64l^4f_2^2 + \dots. \quad (27)$$

Hence we find in the zero-temperature limits

$$\langle r^2 \rangle \approx 1 - \frac{bl}{\pi^2}N, \quad \langle r^4 \rangle = 1 - 2\frac{bl}{\pi^2}N, \quad (28)$$

where $bl \equiv (D-1)\hbar c/\kappa$. For large c , the polymer at zero temperature may appear considerably shorter than expected from the linear extrapolation of the high-temperature behavior to zero temperature.

The quantum effect can be studied most easily by measuring for a polymer of high stiffness κ the peak value of $1 - r$ which behaves like

$$\langle 1 - r \rangle \approx -2lf_1(b) = -2(D-1)\frac{\hbar c}{\kappa}\frac{1}{b}f_1(b). \quad (29)$$

One may plot the function $C(b) \equiv 6\kappa/(D-1)\hbar c\langle 1 - r \rangle$, for which our result implies the behavior shown in Fig. 1 for various link numbers N .

We challenge experimentalists to detect this behavior.

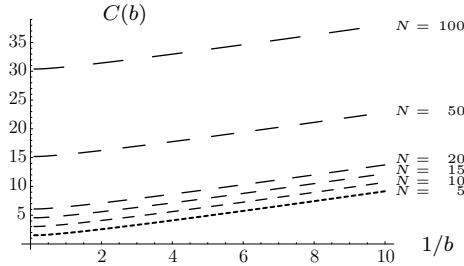


FIG. 1: Temperature behavior of $C(b) \equiv 6\kappa/(D-1)\hbar c\langle 1 - r \rangle$ for various link numbers N . The classical limit of these curves are their straight-line asymptotes starting out at the origin with slope $(6/\pi^2) \sum_{n=1}^N n^{-2}$.

5. Further quantum effects can be observed if the links of the polymer contain a spin $S = 1/2, 1, 3/2, 2, \dots$ the link direction. This can be taken into account by adding the kinetic action (30) a *Berry phase*. For each link $\mathbf{u}_n(\tau)$, it corresponds to the interaction of the particle on the surface of a unit sphere in \mathbf{u} space with a magnetic monopole of quantized charge q lying at the center of the sphere [8]:

$$\mathcal{A}_0 = \hbar S \sum_{n=1}^{N-1} \int_0^{\hbar\beta} d\tau \frac{\mathbf{n} \times \mathbf{u}_n(\tau)}{1 - \mathbf{n} \cdot \mathbf{u}_n(\tau)} \cdot \dot{\mathbf{u}}_n(\tau). \quad (30)$$

The irrelevant Dirac string is chosen to export the magnetic flux of strength S along the \mathbf{n} direction to infinity. This action creates a radial magnetic field $\mathbf{B} = -S\mathbf{u}_n$ on the surface of the sphere. If we assume \mathbf{R} to run along the positive z direction, the small transverse fluctuations \mathbf{q}^T in (7) will take place near the north pole of the sphere and receive an additional magnetic interaction $\hbar S \sum_{n=1}^{N-1} \int_0^{\hbar\beta} d\tau \mathbf{q}_n^T \times \dot{\mathbf{q}}_n^T / 2a$. This will change each factor in the product (17) to a product of two square roots [9]

$$\left[\frac{\sinh K_n K_n^+(0) \hbar c \beta / 2}{\sinh K_n K_n^+(k) \hbar c \beta / 2} \right]^{\frac{1}{2}} \left[\frac{\sinh K_n K_n^-(0) \hbar c \beta / 2}{\sinh K_n K_n^-(k) \hbar c \beta / 2} \right]^{\frac{1}{2}} \quad (31)$$

where

$$K_n^\pm(k) \equiv \sqrt{K_n^2 + k^2 + k_S^2} \pm k_S, \quad k_S \equiv \frac{\hbar c S}{2\kappa a}. \quad (32)$$

the stretched polymer. For arbitrary temperatures, this changes Eqs. (19) and (20) to

$$f_1(b) = -\frac{b}{8\pi^2} \sum_{n=1}^{\infty} \frac{n}{n_S} \left(\coth \frac{nn_S^+ b}{2} + \coth \frac{nn_S^- b}{2} \right), \quad (33)$$

$$f_2(b) = \frac{b^2}{64\pi^4} \sum_{n=1}^{\infty} \left[\frac{2n}{bn_S^3} \left(\coth \frac{nn_S^+ b}{2} + \coth \frac{nn_S^- b}{2} \right) + \frac{n^2}{n_S^2} \left(\coth^2 \frac{nn_S^+ b}{2} + \coth^2 \frac{nn_S^- b}{2} - 2 \right) \right], \quad (34)$$

where $n_S^\pm = n_S \pm \kappa_S$, $n_S \equiv \sqrt{n^2 + \kappa_S^2}$, and $\kappa_S \equiv \hbar c S L / 2\pi \kappa a = k_S L / \pi$. At high temperatures, these become

$$f_1^S(b) \rightarrow -\frac{1}{4\pi^2} \sum_{n=1}^{\infty} \frac{1}{n_S} \left(\frac{1}{n_S} + \frac{1}{n_S^+} \right) = -\frac{1}{12}, \quad (35)$$

$$f_2^S(b) \rightarrow \frac{1}{16\pi^4} \sum_{n=1}^{\infty} \left[\frac{1}{n_S^3} \left(\frac{1}{n_S^-} + \frac{1}{n_S^+} \right) + \frac{1}{n_S^2} \left(\frac{1}{(n_S^-)^2} + \frac{1}{(n_S^+)^2} \right) \right] = \frac{1}{360}. \quad (36)$$

The classical limit is independent of κ_S , as could have been anticipated.

At low temperatures, we obtain for small κ_S to lowest order

$$f_1^S(b) \rightarrow -\frac{b}{4\pi^2} \sum_{n=1}^N \frac{n}{n_S} = -\frac{b}{4\pi^2} \left(N - \frac{\pi^2 \kappa_S^2}{12} \right), \quad (37)$$

$$f_2^S(b) \rightarrow \frac{b}{16\pi^4} \sum_{n=1}^N \frac{n}{n_S^3} = \frac{b}{96\pi^2} \left(1 - \frac{\pi^2 \kappa_S^2}{10} \right). \quad (38)$$

Thus $f_1(b)$ depends only very weakly on κ_S so that the curves in Fig. 1 are practically unchanged by an extra spin S along the links. The spin dependence becomes

visible only in measurements of $f_2(b)$ which can be extracted from suitable combinations of the moments $\langle 1-r \rangle$ and $\langle (1-r)^2 \rangle_c$ obtained by solving Eqs. (25) and (27).

7. Our discussion has shown that at low temperatures quantum fluctuations cause observable effects in polymers. We have calculated these effects for the lowest moments $\langle r^2 \rangle$ and $\langle r^4 \rangle$ of the end-to-end distribution for ordinary polymers as well as for polymers in which each link carries a spin S . In the latter case the polymers are flexible one-dimensional quantum Heisenberg ferromagnets. With the presently available traps and cooling techniques, experimentalists should be able to detect these effects.

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- [6] See Sections 2.12, 3.4, and 15.9.4 in Ref. [3]
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- [8] See Section 8.13 in Ref. [3].
- [9] See Eq. (2.679) in Ref. [3].

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- [1] For a review and references see L. Pitaevskii and S. Stringari, *Bose-Einstein Condensa-*